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Principles of Calorimetric Assay

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21.1 INTRODUCTION

Calorimetry is the quantitative measurement of heat. It measures the transfer of energy from one system to another caused by temperature differences. Applications of calorimetry include measurements of the specific heats of solids and liquids, the heats of vaporization and combustion, and the rate of heat generation (power) from radionuclides. For the last mentioned application, radiometric calorimeters are used. They are specifically designed to measure the power associated with alpha, beta, or gamma decay of radioactive materials. The technique was first used in 1903 to determine the heat produced from radium.

Methods of calorimetry are now being applied with precision and accuracy to the passive nondestructive assay of nuclear materials, especially plutonium and tritium. This chapter discusses the calorimetric assay of plutonium. The important features and advantages of calorimetric assay are listed below (Refs. 1 and 2):

(a) The entire sample can be measured.

(b) The assay is independent of sample geometry (only equilibrium time is affected).

(c) The assay is independent of matrix material composition and distribution, including nominal moisture concentrations.

(d) The assay is independent of nuclear material distribution within the sample, including the effects of sample self-attenuation.

(e) Electric current and potential measurements are directly traceable to National Bureau of Standards (NBS) reference materials.

(f) Calorimetric assay discriminates between uranium and plutonium isotopes in most cases (only plutonium is assayed).

(g) Calorimetric assay is applicable to a wide range of material forms (including metals, alloys, oxides, fluorides, mixed oxides, waste, and scrap). Representative plutonium standards are not needed.

(h) Calorimetric assay is comparable to chemical assay in precision and accuracy if the isotopic composition is well characterized.

(i) Calorimetric assay is a completely nondestructive assay procedure when coupled with high-resolution gamma-ray spectroscopy isotopic analysis.

Calorimetric assay is based on accurate temperature measurements and requires good temperature stability and control. In general the technique is more accurate but less rapid or less portable than other nondestructive assay techniques described in this book. It can often provide accurate reference measurements for improving the calibration of other assay techniques such as neutron coincidence counting (Ref. 3).

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Calorimetric assay is most precise for materials with high plutonium concentrations such as powders, fuel pellets, and metals. Calorimeters are being used extensively for nuclear materials accountability and for shipper-receiver confirmatory measurements of plutonium. When applied to concentrated, homogeneous plutonium-bearing materials, calorimetry is comparable in accuracy to weight plus chemical analysis with precisions approaching 0.1%. For high-density scrap, calorimetry plus gamma-ray spectroscopy can approach a precision and accuracy of 1% if the scrap has homogeneous isotopic composition.

This chapter discusses the principles of heat production, specific power determination, calorimeter types, methods of operation, and basic sources of assay error. Chapter 22, Calorimetric Assay Instruments, describes existing calorimeters of various types, including small calorimeters for laboratory use and bulk assay calorimeters for in-plant applications.

21.2 HEAT PRODUCTION IN RADIONUCLIDES

The energy associated with the spontaneous decay of radioactive isotopes consists of the kinetic energy of the alpha and beta particles emitted, the electromagnetic energy of the gamma rays, and the recoil energy of the daughter product, which collectively is termed the disintegration energy of a particular isotope. If the daughter product is not in the ground state as a result of the decay, additional gamma-ray and internal conversion electron energy will be released when the daughter decays to the ground state. Each radioactive isotope has a specific disintegration energy associated with its particular decay scheme; for example, ^{239}Pu decays to ^{235}U + alpha + 5.15 MeV.

Radiometric calorimeters operate on the principle that almost all of the energy associated with the decay of radioactive materials placed in the sample chamber is absorbed in the form of heat within the calorimeter. The radioactive decay of all uranium and plutonium isotopes generates heat, but only the plutonium isotopes, because of their shorter half-lives and thus higher specific activities, generate heat at a high enough rate (power) to be measured accurately. Most of the plutonium decay energy is released as alpha or beta particles and converted to heat energy through absorption. A small portion is carried away by neutrons and gamma rays, however this portion is generally less than 0.01% of the total decay energy (Ref.1).

Calorimetric assay of plutonium is the process of measuring with a calorimeter the rate of heat released by the radioactive decay of the plutonium and determining the proper analytical factor for converting the calorimetric power measurement to mass. This section describes in detail the production of heat in plutonium. Section 21.3 describes the calculations required to determine the specific power—the factor that relates the power measurement to plutonium mass.

21.2.1 Alpha Particles

The dominant radioactive decay mode of the plutonium isotopes is alpha decay. The mechanism by which heavy particles such as alpha particles transmit their kinetic energy to surrounding material is usually ionization. In its penetration of material until the loss of all of its initial energy, the alpha particle undergoes a large number of "collisions,"

with smaller and smaller amounts of energy loss per collision. These small energy losses are of the order of magnitude characteristic of infrared radiation, that is, heat energy.

The range of alpha particles in various materials relative to their range in air is given by the Bragg-Kleeman rule, Equation 11-2 in Chapter 11. The range of 5- to 6-MeV alpha particles is on the order of 5 μm in common materials. Thus virtually all of the energy released by alpha decay will remain within the sample as heat.

21.2.2 Beta Particles

The determination of energy losses in matter is much more complicated with beta decay or electron capture than with alpha decay. With beta decay, a variety of competing mechanisms are involved: ionization, bremsstrahlung radiation, neutrino production, and conversion electron emission. The energy deposited locally in an absorber in the form of heat is, on the average, one-third of the maximum disintegration energy accompanying the beta decay of a particular radionuclide. The remaining energy is lost from the heat measurement.

The primary mechanism through which low- and intermediate-energy beta particles lose their energy in matter is ionization. Bremsstrahlung is predominant with respect to high-energy beta particles if their kinetic energy is greater than their rest mass (511 KeV). The energy loss resulting from ionization is proportional to the atomic number Z of the absorbing material and increases logarithmically with energy. The energy loss that is due to bremsstrahlung radiation is proportional to Z^2 and increases linearly with energy. The conclusion is that at high energy the energy loss resulting from radiation is predominant. The radiation length is defined as the path length of the absorber in which the electron emerges with 1/e of its initial energy. For a 2-MeV electron, a typical radiation length in plutonium oxide is several millimeters.

Accompanying each beta particle is an antineutrino, which carries with it part of the disintegration energy. Neutrinos are extremely penetrating with respect to matter, so that a portion of the beta emission disintegration energy is not locally deposited.

The emission of conversion electrons is an alternative mechanism to de-exitation of a nucleus by gamma-ray emission. The energy of conversion electrons can also be transferred to surrounding material by ionization or bremsstrahlung.

21.2.3 Gamma Rays

The decay of a radioisotope by the emission of a particle, such as an alpha or beta particle, usually leaves the daughter nucleus in an excited state. A daughter nucleus making a transition gives up excess energy by means of gamma-ray emission, internal conversion, or internal pair production. Of these, gamma-ray emission is the dominant process. Gamma rays emitted from nuclear materials usually have energies ranging from a fraction of an MeV to a few MeV. In this range, gamma rays usually interact with matter by photoelectric effect, Compton scattering, or pair production. If these interactions do not occur within the sample, the energy associated with high-energy gamma-ray emission is not captured by the calorimeter. As indicated earlier, this lost energy is a small percentage of the total disintegration energy of the plutonium isotopes.

21.2.4 Other Emissions

In addition to the primary alpha, beta, and gamma emissions, radionuclides also emit neutrons through the spontaneous fission process. The energy lost through neutron emission is many orders of magnitude less than the total disintegration energy.

Chemical reactions, such as oxidation, and radiochemical processes, such as those associated with fission products in reprocessing plant solutions, are other possible sources of heat. Possible errors from such sources may be estimated by using gamma-ray spectroscopy to detect fission products, by observing any time-dependent power emission, or by comparing calorimetry with other techniques (Ref. 4).

21.3 SPECIFIC POWER DETERMINATION

21.3.1 Definition of Specific Power

Each radioisotope decays at a constant mean rate, λ disintegrations/s, with an energy release of Q MeV. The rate of energy release W for a specific isotope is then given by

$$W(\text{in MeV}) \; = \; QN\lambda \tag{21-1}$$

where N is the number of radioactive atoms present. $N = N_0 m/A$, where N_0 is Avogadro's number, m is the mass of the radioisotope in grams, and A is the atomic weight of the isotope in grams. With $\lambda = 0.6931/T_{1/2}$, where $T_{1/2}$ is the isotope's half-life in years, the power in watts as measured in the calorimeter is given by (Ref. 2)

$$W(\text{in watts}) \; = \; 2119.3Qm/T_{1/2}A. \tag{21-2}$$

If the total energy released per unit time by a radioactive isotope can be collected in a calorimeter and accurately measured, and if the disintegration energy, half-life, and atomic weight of the isotope are known, the mass of the sample can be determined. Equation 21-2 also shows that the power developed in a calorimeter by radioactive decay is directly proportional to the mass of the isotope present:

$$W \; = \; Pm. \tag{21-3}$$

The proportionality constant P is the specific power for the given isotope, measured in watts of power per gram of isotope present. The specific power of a single isotope can be calculated directly from Equation 21-2 if the appropriate parameters are known (computational method) or it can be determined experimentally with Equation 21-3 (empirical method). The procedures for both the computational and empirical methods are detailed in Ref. 4.

Specific power values and other nuclear constants for the isotopes of plutonium are summarized in Table 21-1 (Ref. 4). Note that the specific power of [238]Pu is much greater ($\sim$250 times) than that of [239]Pu because of the shorter alpha half-life of [238]Pu. The specific power of [241]Am is also considerably larger than that of [239]Pu, so the [241]Am content at the time of calorimetric assay is very important. Americium-241 content

Table 21-1. Specific power values for the plutonium isotopes (Ref. 4)

Radio-nuclide	Disintegration Energy Release Q(MeV)	Principal Decay Mode	Total Half-Life $T_{1/2}$ (yr)	Specific Power P (mW/g)	Specific Power Std. Deviation (mW/g)
^{238}Pu	5.592	alpha	87.74	567.57	0.26
^{239}Pu	5.243	alpha	24 119	1.9288	0.0003
^{240}Pu	5.255	alpha	6 564	7.0824	0.002
^{241}Pu	0.0055	beta	14.348	3.412	0.002
^{242}Pu	4.985	alpha	376 300	0.1159	0.0003
^{241}Am	5.640	alpha	433.6	114.2	0.42

increases with time because ^{241}Am is produced by the decay of ^{241}Pu, and thus the power from a plutonium sample also increases as a function of time. For the decay of ^{241}Pu to ^{241}Am within the sample, both the parent nucleus and the daughter nucleus contribute to the total power. The contribution of ^{241}Am to the total power is described by Equation 21-11 at the end of Section 21.3.2.

21.3.2 Effective Specific Power

Because actual plutonium samples contain differing amounts of the various isotopes listed in Table 21-1, the total power is the sum of the power from each isotope:

$$W = \sum_{i=1}^{n} m_i P_i \qquad (21\text{-}4)$$

where m_i is the mass of the ith isotope, P_i is the specific power of the ith isotope, and the sum n is taken over the plutonium isotopes and ^{241}Am. If R_i is defined as the mass fraction m_i/M of the ith isotope, where M is the total mass of all the plutonium isotopes, then

$$W = M \sum_{i=1}^{n} P_i R_i \ . \qquad (21\text{-}5)$$

For calorimetric assay, the important factor is the effective specific power P_{eff}, which is expressed in watts per gram of plutonium and is defined by

$$P_{eff} = \sum_{i=1}^{n} P_i R_i \ . \qquad (21\text{-}6)$$

In terms of effective specific power, the total mass of all the plutonium isotopes is given by

$$M = W/P_{eff} \ . \qquad (21\text{-}7)$$

The mass of each particular isotope is given by

$$m_i = R_i W/P_{eff} .$$
(21-8)

To obtain accurate calorimetric assays, very good values for the effective specific power of the sample must be known. The effective specific power can be determined by either the empirical method or the computational method (Ref. 4):

(a) *The Empirical Method.* The empirical method of determining effective specific power is well suited to discrete batches of process materials or to cases where the computational method is difficult to apply because the abundances of [238]Pu and [241]Am are not well known. This method requires both a chemical and a calorimetric analysis of the sample; the calorimetric analysis determines the total power produced by the sample, and the chemical analysis determines the total amount of nuclear material in the sample. Equation 21-7 can then be used to calculate the effective specific power.

(b) *The Computational Method.* The computational method for determining effective specific power is appropriate when very accurate isotopic determinations can be made. If radionuclide abundances R_i can be measured and the specific power values P_i are known for each radionuclide, then the effective specific power for a given isotope mix can be calculated from Equation 21-6.

The relative abundances of the radionuclides can be determined nondestructively by gamma-ray spectroscopy (See Chapter 8) or destructively by mass spectroscopy (Refs. 5 and 6). Destructive methods must include a technique for the determination of [241]Am. Plutonium-238 abundance is preferably measured by alpha-particle spectrometry (Ref. 4).

The isotopic mass fractions must be accurately known and corrected for decay to the date of the calorimeter power measurement because the effective specific power is a time-dependent quantity. The corrections for radionuclide decay can be made either by establishing a power growth curve for the sample over a period of at least 30 days or by calculating a correction for growth and decay from the previously determined isotopic abundances. According to Ref. 4, if the power curve method is used, "a minimum of three points should be made to establish a straight line showing power as a function of time. The curve should be checked after an additional 30 days."

The correction for radionuclide decay based on calculation from previously measured radionuclide abundances is usually the easiest approach, as in Equation 21-9.

$$W = M \sum_{i=1}^{n} P_i R_i(t) .$$
(21-9)

Equation 21-9 is the same as Equation 21-5 except that $R_i(t)$ expresses the time dependence of the mass fractions. For the plutonium isotopes,

$$R_i(t) = R_i(t_I)exp[-\lambda_i(t-t_I)]/F(t)$$
(21-10)

where $R_i(t)$ = mass fraction of the ith plutonium isotope at time t
t_I = time of plutonium isotopic analysis
λ_i = decay constant of the ith plutonium isotope

$$F(t) = \sum_{i=1}^{n-1} R_i(t_I) \exp[-\lambda_i(t-t_I)] \quad ,$$

summed over the plutonium isotopes only.

For the daughter nucleus ^{241}Am, the mass fraction is due to both the decay of ^{241}Am and the ingrowth from beta decay of ^{241}Pu:

$$R_A(t) = \frac{F(t_A)}{F(t)} R_A(t_A) \exp[-\lambda_A(t-t_A)] \tag{21-11}$$

$$+ K_1 K_2 \frac{R_1(t_I)}{F(t)} \frac{\lambda_1 \exp[-\lambda_1(t_A-t_I)]}{\lambda_1-\lambda_A} \left\{ \exp[-\lambda_A(t-t_A)] - \exp[-\lambda_1(t-t_A)] \right\}$$

where $R_1(t_I)$ = mass fraction of ^{241}Pu determined at time t_I
$R_A(t)$ = mass fraction of ^{241}Am relative to total plutonium at time t
t_A = time of americium analysis
λ_A = decay constant of ^{241}Am
λ_1 = decay constant of ^{241}Pu
K_1 = 0.9999754, ^{241}Pu branching ratio to ^{241}Am
K_2 = 0.999999905, ^{241}Am/^{241}Pu atomic mass ratio.

Lastly, if the total mass of plutonium is known at some time t_m, the mass at any future date is

$$m(t) = m(t_m) F(t)/F(t_m) \quad . \tag{21-12}$$

21.4 HEAT MEASUREMENT BY CALORIMETRY

A calorimeter consists of a container with a temperature sensor in which the thermal phenomenon under investigation is carried out. In general the container is coupled to its environment by walls that have some thermal resistance. These basic features are illustrated in Figure 21.1 (Ref. 7). Heat liberated in the internal cavity raises its temperature and causes heat to flow across the thermal resistance into the environment according to Equation 21-13:
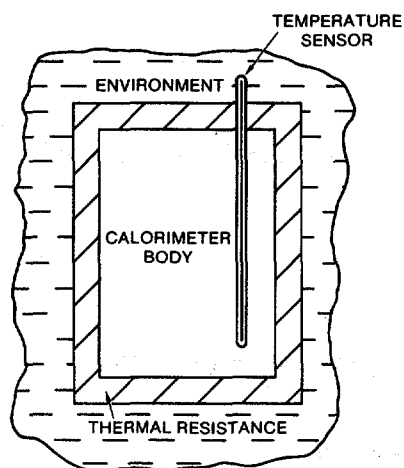
$$\frac{dQ}{dt} = k(T_{cal} - T_{env}) \tag{21-13}$$

where Q = heat energy
k = thermal conductivity
T_{cal} = internal calorimeter temperature
T_{env} = external environment temperature.

Depending on the magnitude of this heat exchange, the calorimeter can be classified as adiabatic or isothermal.

Fig. 21.1 *The basic features of a calorimeter are its body or internal cavity, a temperature sensor, a thermal resistance gap, and the external environment. (Figure courtesy of Mound Laboratory.)*

21.4.1 Adiabatic Calorimeters

In general, calorimeters are designed with a large thermal resistance between the cavity and its environment. As a result, almost all of the heat produced in the calorimeter body is retained, causing its temperature to increase. By measuring the temperature increase ΔT, one can determine the amount of heat energy released from the formula $Q = C \Delta T$, where C is the heat capacity. If the source of heat gives rise to a constant rate of heat production, the internal temperature T_{cal} will rise at a constant rate. If the source of heat is finite, the internal temperature will level off.

An efficient type of adiabatic calorimeter is one designed such that T_{env} is continuously adjusted to match T_{cal} so that the rate of heat transfer $dQ/dt = 0$. This adjustment is accomplished with a regulator that responds to any difference between the two temperatures. Adiabatic calorimeters are best suited to the study of processes such as chemical reactions where it is important to measure the total integrated heat production. Adiabatic calorimeters are not used for the assay of radionuclides because the internal temperature would continue to rise indefinitely.

21.4.2 Isothermal Calorimeters

If the thermal resistance between the sample cavity and the environment is small, the heat produced in the calorimeter is transferred to the surrounding environment. For a sample that produces heat at a constant rate, the entire system will reach an equilibrium condition in which the rate of heat transfer to the environment is equal to the rate of heat production in the sample. The rate of heat transfer is directly proportional to the

temperature difference between the sample chamber and the environment, as described by Equation 21-13, where the thermal conductivity k depends on heat path length, material, and surface shape. It is important that the value of k remain constant because the measurement of the rate of heat transfer is essentially a precision temperature measurement. The value of k is determined for a given calorimeter by calibration.

The calorimeter is classified as isothermal if the sample chamber is held at a constant temperature. If the calorimeter is also designed so that the thermal resistance between the sample chamber and the heat sink is moderate, it is classified as a heat flow calorimeter.

Radiometric calorimeters—those designed for the calorimetric assay of radioactive isotopes—are usually heat flow calorimeters because plutonium samples emit heat at an almost constant power level as a result of the spontaneous decay of their radioactive isotopes. The different types of calorimeters used for plutonium assay that are described in the following section are all heat flow calorimeters.

21.5 TYPES OF HEAT FLOW CALORIMETERS

Although calorimetric assay of plutonium is usually performed by a heat flow calorimeter, no universal calorimeter design is suitable for all applications. Each system is custom designed with many specifications in mind, as described in Section 22.1.2 of Chapter 22. Depending on the specific requirements, the final design may employ features of one or more of the calorimeter types described in this section: twin bridge, over/under bridge, and gradient bridge.

21.5.1 Common Electrical Features

One common feature of modern calorimeters is the precise measurement of temperature by electrical means. The determination of total sample power is then basically an electrical measurement of the temperature difference between the sample chamber and the environmental heat sink or reference chamber.

In twin-bridge calorimeters, both the sample chamber and the reference chamber have two nickel wire windings whose resistance is a function of temperature. The four windings are connected as a transposed-arm wheatstone bridge and are supplied with a constant current, as illustrated in Figure 21.2 (Ref. 7). With this arrangement, the temperature difference between the sample and reference chambers is directly proportional to the bridge potential BP.

With no sample in the calorimeter, a small bridge potential BP_0 (in microvolts, μV) may be observed because of variations in the resistances of the nickel windings. When a reference electrical heat source or radioisotope standard that emits a power level of W_R watts is placed in the sample chamber, the bridge potential will reach an equilibrium value BP_R (μV). The sensitivity S of the calorimeter in microvolts per watt is

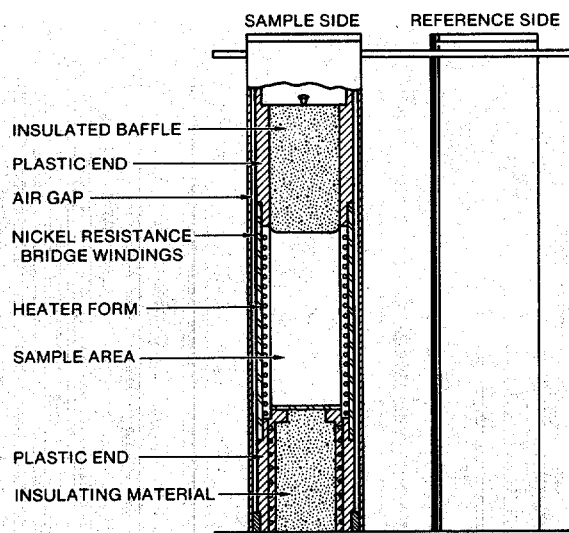$$S(\mu V/W) = (BP_R - BP_0)/W_R .$$ \hfill (21-14)
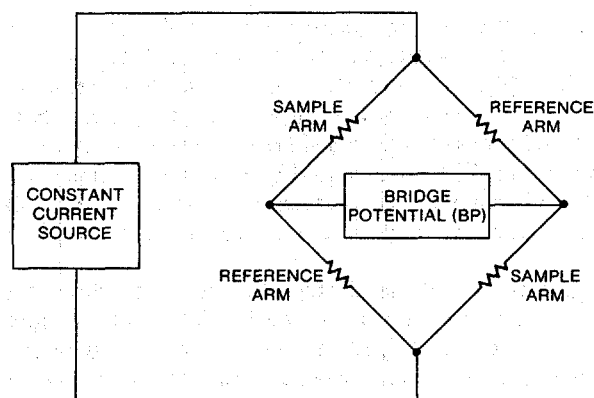
Fig. 21.2 *A wheatstone bridge circuit is used to accurately measure the temperature difference between the sample and reference parts of a calorimeter. (Figure courtesy of Mound Laboratory.)*

21.5.2 Full Twin-Bridge Calorimeters

To increase calorimetric accuracy, nearly all calorimeters can be arranged as twin calorimeters. The most common example is the isothermal twin-bridge calorimeter developed at Mound Laboratory and used extensively for in-plant assays (Ref. 8). Figure 21.3 shows a cross section of this calorimeter type, and Figure 21.4 is a photograph of a full twin-bridge calorimeter without its surrounding water bath.

The full twin-bridge design consists of two identical thermal elements, sample side and reference side, each separated from the outer wall by an air gap or solid gap that serves as the thermal resistance. Each thermal element has heater wires wrapped around its sample chamber for calibration purposes. Axial heat loss from the sample chamber is minimized by the use of plastic end caps with Styrofoam baffles and metal plates to provide a thermal short from the sample to the calorimeter walls. Two resistance thermometers consisting of thin nickel wire are wound over the entire length of each thermal element to provide an accurate temperature measurement independent of variations in heat flow (Ref. 8).

For operation, the twin calorimeter is immersed in a water bath whose temperature is held constant to about one millidegree. In addition, the use of two identical thermal elements yields a difference signal that is 10 to 100 times more stable than the environmental bath. When a sample is placed in the chamber, the temperature rises until heat losses through the nickel windings, thermal gap, and outer jacket to the water bath equal the heat generated by the sample. When this equilibrium is attained, the temperature difference measured by the bridge potential is proportional to the amount of heat being generated. Precise heat flow calorimeters of this type are designed and

SAMPLE SIDE REFERENCE SIDE

INSULATED BAFFLE

PLASTIC END

AIR GAP

NICKEL RESISTANCE
BRIDGE WINDINGS

HEATER FORM

SAMPLE AREA

PLASTIC END

INSULATING MATERIAL

Fig. 21.3 *Cross section of a typical isothermal twin calorimeter with two identical thermal cells, one for the sample and one for reference. (Figure courtesy of Mound Laboratory.)*

constructed so that the thermal paths between the sample chamber and the environment remain constant. Additional care is taken to keep the temperature of the environment constant and to minimize the heat distribution error associated with the location of the sample in the chamber.

The twin-bridge calorimeter provides the best precision, accuracy, sensitivity, and long-term stability for power measurements because of the internal cancellation of many thermal effects. However, the two thermal elements and the environmental bath result in an instrument that is larger and requires more floor space than other designs. Twin-bridge calorimeters have been designed for sample sizes ranging from 1 to 30.5 cm in diameter with an upper limit dictated only by nuclear criticality safety considerations and a lower limit in the range of 0.1- to 0.2-g ^{239}Pu/L (Ref. 8). An application of a twin-bridge calorimeter is described in Section 22.4.1 of Chapter 22.

21.5.3 Over/Under Bridge Calorimeters

In the over/under design, the sample cell is mounted above a somewhat shortened reference cell (Ref. 7), as illustrated in Figure 21.5. Both cells share a single isothermal water jacket that is smaller than the environmental bath used by the twin-bridge calorimeter. The over/under bridge design requires less floor space, but is taller. Also, the over/under design can be used to build a transportable calorimeter. The calorimeter shown in Figure 21.5 can be mounted on a mobile cart along with its circulation bath.
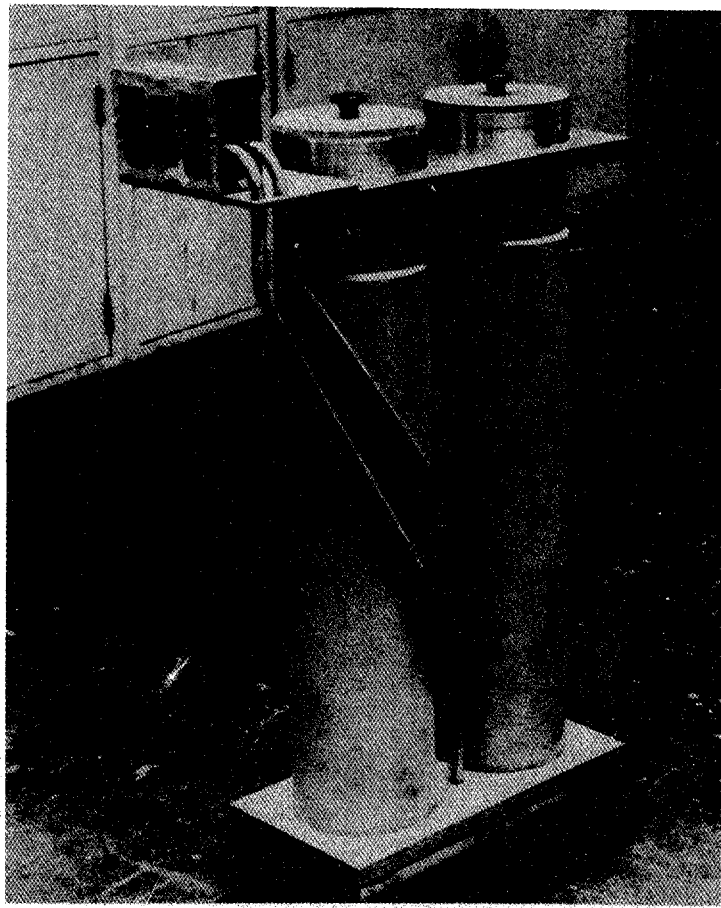
Fig. 21.4 *View of an actual twin-bridge calorimeter without its surrounding*
water bath. (Photograph courtesy of Mound Laboratory.)

The over/under bridge calorimeter has size and cost advantages over the twin-bridge design and provides cancellation of some thermal effects. However, the accuracy is not as good as the full twin-bridge calorimeter. Examples of over/under bridge calorimeters are given in Sections 22.3.1 and 22.4.2 of Chapter 22.

21.5.4 Gradient Bridge Calorimeter

The gradient bridge calorimeter (Figure 21.6) consists of a series of concentric cylinders, with the sample cell cylinder inside the reference cell cylinder (Ref. 7). The gap between the reference cell cylinder and the sample cell cylinder determines the sensitivity of the calorimeter. Outside the reference cylinder is a jacket that provides a uniform
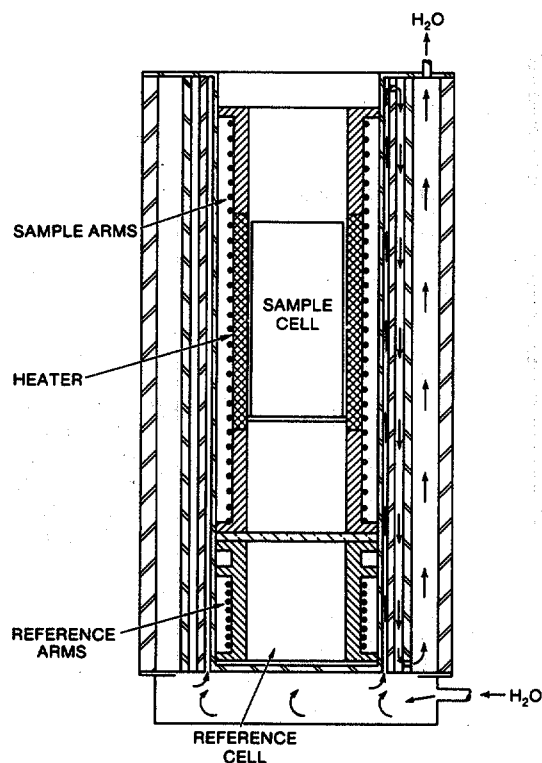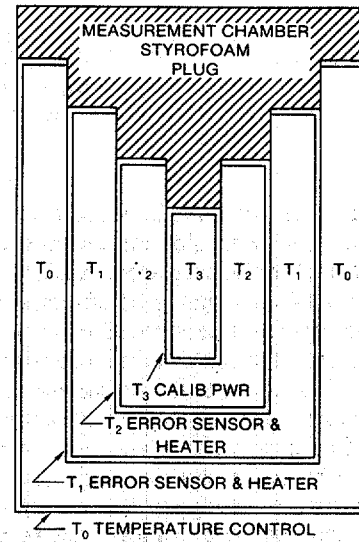
Fig. 21.5 *A transportable calorimeter of the over/under bridge design with the sample cell above the reference cell and a thin water jacket. (Figure courtesy of Mound Laboratory.)*

thermal heat sink. The jacket is in contact with a thin circulating water bath. This design leads to small size and low material and fabrication costs. The gradient design is well suited for transportable versions or glovebox installations, or for large samples where overall bulk should be minimized. The gradient calorimeter is usually operated in the constant temperature servo-control mode described in Section 21.6.3 below. A Mound gradient bridge calorimeter design is described in Section 22.4.4 of Chapter 22.

The isothermal air chamber calorimeter developed by Argonne National Laboratory is a version of the gradient design that does not require a water bath (Refs. 9 and 10). This calorimeter (Figure 21.7) is described in Ref. 10 as "...a constant temperature oven composed of a series of concentric chambers. Each of these chambers is constructed from an aluminum cylinder upon which resistive heating coils and heat sensors are mounted. The cylinders are separated from one another by high thermal-resistance material. The ends of the cylinders are similarly protected by nonconducting plugs and by pancake-type heater coils. Alternating zones of high and low thermal conductivity in

EPOXY THERMAL GAP

REFERENCE ARMS

SAMPLE AREA

HEATER FORM

SAMPLE ARMS
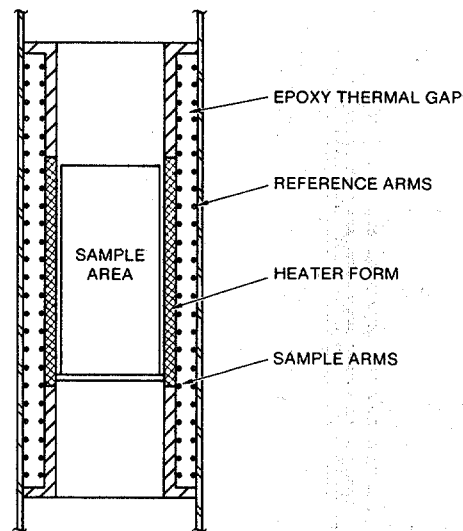
Fig. 21.6 *Cross section of a gradient bridge calorimeter design. The environmental heat sink, which would be small or just an air chamber, is not shown. (Figure courtesy of Mound Laboratory.)*

MEASUREMENT CHAMBER
STYROFOAM
PLUG

T_0 T_1 T_2 T_3 T_2 T_1 T_0

T_3 CALIB PWR

T_2 ERROR SENSOR & HEATER

T_1 ERROR SENSOR & HEATER

T_0 TEMPERATURE CONTROL

Fig. 21.7 *Cross section of an air chamber calorimeter, a version of the gradient bridge calorimeter. (Figure courtesy of Argonne National Laboratory.)*

this manner tends to minimize the effects of localized external temperature changes. A temperature profile is established within the calorimeter to eliminate axial heat flow and to ensure that a negative radial temperature gradient is maintained. In the schematic drawing (Figure 21.7), the electronic feedback control circuits will maintain the relation $T_3 > T_2 > T_1 > T_0 > T_{ambient}$. The inner two cylinders (T_3, T_2) act as the measurement chamber. The calorimeter-supplied electrical power is adjusted to maintain the temperature difference between these cylinders to ± 20 microdegrees." Calorimeters of this type have been used to measure sealed containers of bulk materials with up to 3 kg of plutonium, mixed-oxide fuel pellets, and fuel rods up to 4 m in length. Examples are given in Sections 22.2.2, 22.3.2, and 22.5.1 of Chapter 22.

21.6 METHODS OF OPERATION FOR HEAT FLOW CALORIMETERS

21.6.1 Replacement Method

In this mode of operation the sample to be measured is placed in the calorimeter and allowed to come to thermal equilibrium. The temperature difference between the calorimeter and the heat sink is determined from the bridge potential. Then the sample is removed and the calorimeter is heated electrically until the same equilibrium temperature difference is obtained. The sample power can be determined from the known power supplied by the heater that replaced the sample. The same chamber of the calorimeter is used for both the sample run and the heater run.

The replacement method consists of the following steps (Refs. 7 and 8):

(1) A bridge potential BP_0 is measured with the sample chamber empty, zero heater power, and the environmental tank under temperature control. BP_0 is normally measured periodically, not for each sample.

(2) The sample to be assayed is placed in the calorimeter and its equilibrium bridge potential BP_S is determined.

(3) The sample is then removed and the heater current required to replace the sample power is calculated. The heater power required is approximately

$$W_H(\text{approx}) = (BP_S - BP_0)/S \tag{21-15}$$

where S is the sensitivity of the calorimeter as determined earlier with Equation 21-14. The required heater current is then calculated. The problem of power dissipation in the wires leading to the heater can be minimized in the twin design calorimeter by running the wires through both the sample and reference chambers so that the effects cancel.

(4) The heater current is applied to the sample chamber until the equilibrium bridge potential BP_H can be determined. Also, the actual exact heater power W_H is calculated from the measured heater current and voltage.

(5) The power of the unknown sample is then

$$W_S(\text{watts}) = W_H + (BP_S - BP_H)/S \ . \tag{21-16}$$

The above procedure is illustrated in Figure 21.8, which also shows the additional complexity introduced by slow drifts in the instrument.
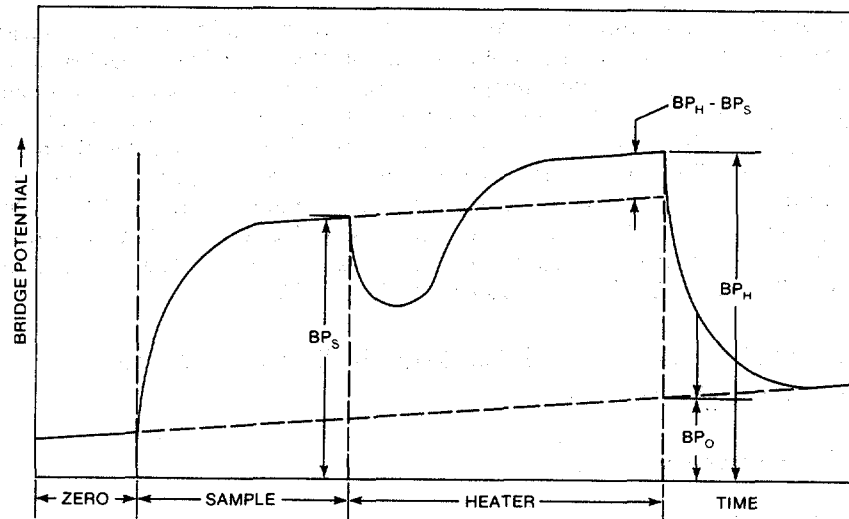
Fig. 21.8 Calorimeter bridge potential as a function of time as observed during the replacement method of operation. The upward slopes illustrate the additional complexity introduced by gradual instrument drifts. (Figure courtesy of Mound Laboratory.)

21.6.2 Differential Method

A twin-bridge or over/under bridge calorimeter can be operated in the differential mode in which electrical heat in the reference side is compared directly to sample heat from the sample side. Because the sample run and the heater run are simultaneous, assays can be made in about half the time required for the replacement method. In practice this time savings is realized only when the sample power is known in advance to about 1%. Thus the differential method is most useful when many samples of approximately the same size are to be assayed. For samples of unknown size this method is only slightly faster than the replacement method (Ref. 8).

When the differential method is used, the sample power at equilibrium is given by

$$W_S(\text{watts}) = W_H + (BP_S - BP_M)/S \quad . \tag{21-17}$$

BP_M is a bridge potential calculated from mW_H, where m is a constant slope. The quantity $(BP_S - BP_M)$ is zero if the heater power exactly matches the sample power; if not, this quantity compensates for small differences between the two sides. The slope m is determined during calibration by running current through the sample and reference heaters in series (Ref. 8).

21.6.3 Constant Temperature Servo-Control Method

In this mode of operation both the sample chamber and the environmental bath are held at constant temperature by a servo-control mechanism. Heater power is used to maintain the sample chamber at a higher temperature than the bath. When a sample is placed in the calorimeter, the servo-controller reduces the heater power by the amount of the sample's power to hold the chamber at constant temperature. This method, also called the isothermal method, may be used with any calorimeter bridge design. Use of the constant temperature method typically reduces assay time by one-third to one-half because the time required to reach equilibrium depends principally on the thermal resistance and heat capacity of the sample and less on the calorimeter body.

Before samples are assayed by the constant temperature method, the baseline power level is set 10 to 20% above the estimated wattage of any calibration standards or actual samples. A baseline power run is made to establish the empty chamber equilibrium power level W_0. This run takes less time than a sample assay because no mass is in the chamber.

When a radioactive sample is placed in the calorimeter, the heater power drops as the servo-controller tries to maintain a constant temperature in the chamber. The new equilibrium power level is W_C, and the sample power is

$$W_s(\text{watts}) = W_0 - W_C \ . \tag{21-18}$$

Constant temperature control of the calorimeter can be maintained by analog or digital circuits. Digital circuits have the advantage of requiring no adjustments to Equation 21-18 to correct for systematic errors that occur in analog systems.

The constant temperature servo-control method is one of the fastest methods of calorimeter operation, especially when used with "pre-equilibration" of the sample in a separate temperature-controlled environment.

21.7 ASSAY TIME CONSIDERATIONS

The time necessary to complete a calorimetric assay of a radioactive sample is dependent on a variety of factors that influence the time necessary for the system to attain steady-state conditions. These factors include the following:

(a) The type of heat flow calorimeter—twin-bridge, over/under bridge, or gradient bridge.

(b) The thermal resistance and heat capacity of the material used for calorimeter construction and the material the sample is composed of.

(c) The quality of calorimeter construction—tightness of fit, uniformity of air gaps, and so forth.

(d) Physical size of the calorimeter sample chamber and the diameter of the sample.

(e) Sample packaging—location of heat sources inside the package, presence of void spaces, and so forth.

(f) Method of calorimeter operation—replacement, differential, or constant temperature servo-control.

(g) Use of sample preconditioning.

(h) Use of end-point prediction techniques.

(i) Required assay accuracy.

Calorimetric assay of well-characterized small samples may be completed in less than one hour. On the other hand, bulk samples of product or scrap materials require calorimetric assay times of 4 to 16 h to reach thermal equilibrium. Table 21-2 (from Ref. 8) gives a few examples of assay times for a twin-cell, water bath calorimeter. Poor sample packaging consisted of plastic bags and lead shot; good packaging consisted of copper shot. A more complete summary of typical assay times is given in Ref. 1. Some of the factors and techniques that affect assay time are discussed below.

Table 21-2. Some assay times for a twin-bridge calorimeter (Ref. 8)

Assay Conditions	1.0% Equilibrium Time (h)	0.1% Equilibrium Time (h)	0.01% Equilibrium Time (h)
Heater only, no sample, no temperature servo-control	2.8	3.6	4.8
Poorly packaged sample, no temperature servo-control	8.1	10.2	13.1
Well-packaged sample, no temperature servo-control	5.2	6.3	8.0
Poorly packaged sample, constant temperature servo-control	4.7	6.1	8.0
Poorly packaged sample, constant temperature servo-control, sample pre-conditioned	0.8	1.6	3.0

21.7.1 Calorimeter Design and Operating Method

The physical dimensions and thermal properties of a given calorimeter affect both the equilibrium time and the sensitivity. Decreasing the thermal resistance of a calorimeter will reduce the time required to come to equilibrium, but it will also reduce the observed bridge potential and (from Equation 21-14) the sensitivity. Because reduced sensitivity will lead to reduced accuracy, the choice of calorimeter design must reflect a trade-off between assay time and assay accuracy for the particular sample range. The composition and dimensions of the gap between the sample and the calorimeter wall are important factors.

The replacement method of calorimeter operation is generally the slowest mode of operation because three distinct calorimeter runs are required to complete an assay: a sample run, a heater run, and a periodic baseline (BP_0) run. The differential method,

which can be used with twin-bridge calorimeters, requires only two calorimeter runs because the electrical heat in the reference chamber is constantly compared to the heat developed by the sample. This mode of operation reduces the time necessary for assay completion.

The constant temperature servo-control mode of operation, or isothermal mode, is well suited for reducing assay time; when the calorimeter body is maintained in an equilibrium state, the effect of its time constant is minimized and the assay time is principally dependent on the thermal time constant of the sample. Assay time can be reduced further if the sample temperature is pre-equilibrated to the temperature of the calorimeter, as described in the next section.

21.7.2 Sample Preconditioning

Preconditioning of the sample to about the internal temperature of the calorimeter can be used with the constant temperature servo-control method to reduce assay time, as indicated in Table 21-2. Preconditioning can be used alone or in conjunction with the end-point prediction technique described in the next section. When the sample is first placed in a separate preconditioning water bath and then placed in the calorimeter, the time required to reach equilibrium is reduced because only the sample itself needs to equilibrate to a steady-state heat flow. The gradient gap is already at a steady-state heat flow with respect to the heat sink, and the heater power will reach the equilibrium power level more rapidly.

Several advantages and disadvantages are associated with preconditioning (Ref. 7). The primary advantage is increased throughput. The preconditioning bath can be designed to accommodate more than one sample, and it can be used overnight to prepare samples for assay the next day. The disadvantages are that additional floor space, electronics, and operator action are required. Also, the preconditioning bath temperature must be carefully maintained near the internal temperature of the calorimeter. Any change in the calorimeter's baseline power level will require adjustment of the preconditioning bath temperature.

21.7.3 End-Point Prediction

Prediction of equilibrium is a mathematical technique for reducing calorimeter assay time without affecting calorimeter sensitivity or sample packaging. The technique is applicable to a variety of calorimeter types. Equilibrium values can be predicted reliably with a time savings of about 50% (Refs. 11 and 12).

End-point prediction is based on the principle that the calorimeter's response function is dominated by a single exponential of the form

$$Y = A + Be^{-\lambda t} \tag{21-19}$$

where Y is the time-dependent calorimeter output, A is the equilibrium output signal, B is a scaling constant, and λ is the final thermal decay constant of the calorimeter and its sample (Ref. 11). A calorimeter actually consists of different thermal regions, each having different values for thermal resistance R_i and heat capacity C_i, as illustrated in
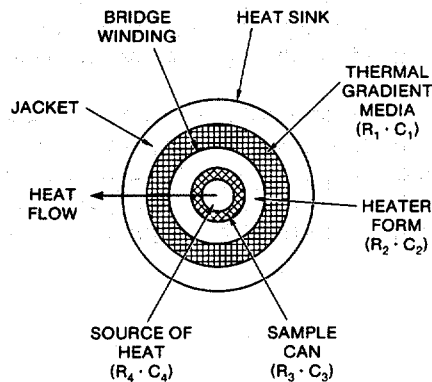
Fig. 21.9 Radial cross section of an idealized calorimeter showing four regions, each having different values for thermal resistance R_i and heat capacity C_i. (Figure courtesy of Mound Laboratory.)

Figure 21.9. The differing thermal properties of each region determine the time required for each region to come to equilibrium with its surroundings. The time required for the entire calorimeter to reach equilibrium is a sum of several exponential response functions. Because the end-point prediction technique is based on the use of Equation 21-19 with a single exponential, the amount of time saved depends on the validity of this approximation. Samples that are poorly packaged, with high thermal resistance or high heat capacity, will be assayed with less time savings.

The procedure for calculating the equilibrium output signal A requires determination of the output signal Y at regular time intervals during the assay (Ref. 7). The values for Y are smoothed and fitted to Equation 21-19 and a value for A is calculated. This procedure is repeated at regular intervals as the assay progresses and as more determinations of Y become available. Figure 21.10 illustrates this process. When the predicted values for A show zero slope within the expected standard deviation, the run is complete. The assay is terminated before the calorimeter actually reaches equilibrium.

21.8 CALORIMETER CALIBRATION

Accurate calibration is needed to relate the observed calorimeter output power to known power values. Two types of standards are commonly used for calibration purposes: electrical and radiometric heat sources. Regardless of the calibration method used, traceability to NBS-certified electrical or radiometric standards is essential (Ref. 4).

21.8.1 Electrical Calibration

Electrical calibration techniques are applicable to calorimetric methods in which heater power either duplicates or replaces sample power (Ref. 4). The power generated in an electrical heater is given by the product of the voltage across the heater and the current through the heater. To calibrate the heater, the current can be determined by measuring the voltage across a standard resistor. This calibration yields the relationship
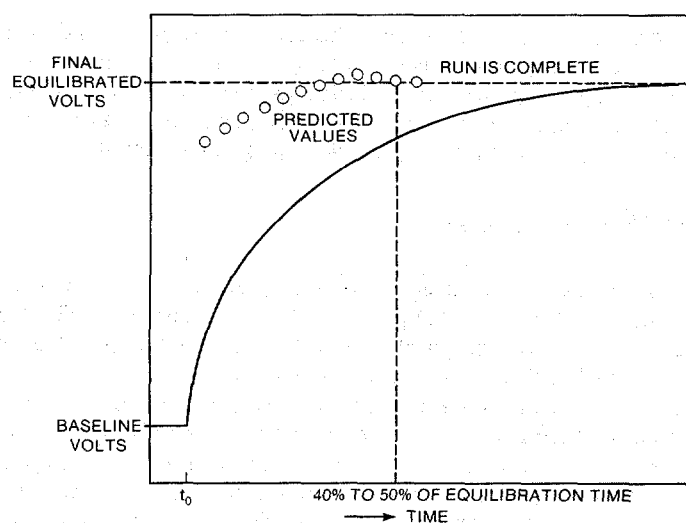
Fig. 21.10 *Graphical representation of the end-point prediction technique. The run is complete when the predicted values show zero slope within the expected standard deviation. (Figure courtesy of Mound Laboratory.)*

between bridge potential and sample power: the calorimeter sensitivity (Equation 21-14). The result is a sensitivity curve as a function of sample power.

Accurate electrical calibration requires that the electrical heater produce the identical change in calorimeter output as an equivalent amount of power from a sample (Ref. 4). This implies that the location of the heater relative to the temperature-measuring device should be the same as that of the radioactive sample. The error associated with this factor is referred to as the heat distribution error. To determine the extent of this error, it is recommended that a small sample be placed at various locations within the chamber and its output measured with respect to location. (One of the radiometric heat standards discussed in the next section would be ideal for this purpose.) Another source of error in electrical calibration is power loss in the heater leads of single-cell calorimeters. The technique for correcting for heater-lead errors is described in Ref. 4.

21.8.2 Calibration with Radioactive Heat Sources

Calibration with radioactive heat sources is a simpler technique and usually preferable because it covers all aspects of calorimeter operation. Standard $^{238}PuO_2$ heat sources that are traceable to NBS reference materials are available from Mound Laboratory in the range 0.04 mW to 100 W (Ref. 7). The sources are compact, and the power output as a function of time can be calculated. The heat sources should span the range of actual sample powers.

In the calibration procedure, the radioactive heat sources are placed in the calorimeter sample chamber in the same manner as the unknown samples. The calorimeter output signal is measured using the known power of each standard heat source. These data are used to generate a calibration curve and an associated sensitivity curve just as in the electrical case. Additional details on this procedure are given in Ref. 4.

21.9 SOURCES OF ERROR

As described in Section 21.3, determination of plutonium content is a two-step process: determination of calorimetric power and determination of effective specific power either by empirical or computational methods. The sources of error in this process are summarized in Table 21-3 (Refs. 4, 7, and 13).

Sources of error in the power determination include (1) imprecision of the calorimeter system—the variance of the system response as a result of variations in room temperature, bath temperature, humidity, sample weight, sample loading and unloading stresses, and so forth; (2) heat distribution error—the variance of the system response resulting from spatial distribution of the sample in the sample chamber; (3) calibration error—the variance of the system response to calibration method and standards; and (4) interference error—heat production from interfering processes such as fission product reactions or chemical reactions.

Sources of error in the determination of effective specific power depend on the method used for this determination: empirical or computational. If the empirical method is used, the possible sources of error are (1) errors in determination of sample power and (2) errors in determination of the content of the plutonium sample. When the computational method is used for determination of effective specific power, the error sources are (1) errors in determination of the sample's isotopic composition and (2) uncertainty in the specific power values (see the last column of Table 21-1). The total assay uncertainty may be estimated by combining the error in the calorimeter power determination with the uncertainty in the effective specific power:

$$\sigma(Pu) = \sqrt{\sigma^2(W) + \sigma^2(P_{eff})} \tag{21-20}$$

The error magnitudes given in Table 21-3 are typical values; in practice, actual values may be quite different. In particular, the errors associated with the determination of isotopic composition depend on the technique used. For concentrations below 0.1%, the errors quoted are typical of radiometric results for [238]Pu and [241]Am. For concentrations of 0.1 to 1%, the minimum error for mass spectrometric determination is 1%; for concentrations greater than 20%, the minimum error is 0.3%. If the isotopic composition is determined by high-resolution gamma-ray spectroscopy, errors for the major plutonium isotopes are in the range of 0.1 to 10%. Errors in the determination of effective specific power are in the range of 0.3 to 1.0% in 1- to 4-h counting times (Ref. 14 and Chapter 8). Generally, the precision of the calorimeter power measurement is better than the uncertainty associated with the determination of effective specific power.

Table 21-3. Sources of error in calorimetric assay (Refs. 4, 7, and 13)

Error Source	Approximate Magnitude (%)
Power Measurement	
Calorimeter imprecision	<0.1
Heat distribution error	<0.1
Calibration error	<0.1
Interference error	<0.1
Effective Specific Power Determination	
Empirical method	
Sample power	<0.2
Sample plutonium content	<0.2
Computational method	
Isotopic composition	
Concentration <0.1%	2-5
Concentration >0.1%	1.5
Concentration >1%	0.5
Concentration >20%	0.3
Specific power uncertainty	<0.1

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